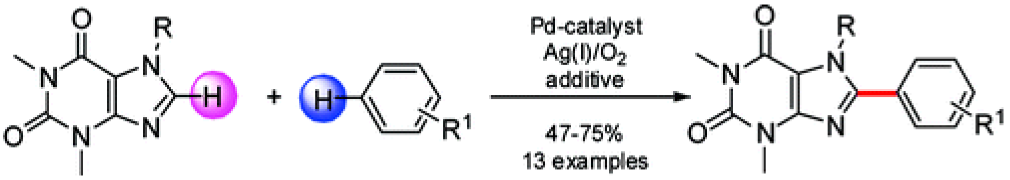
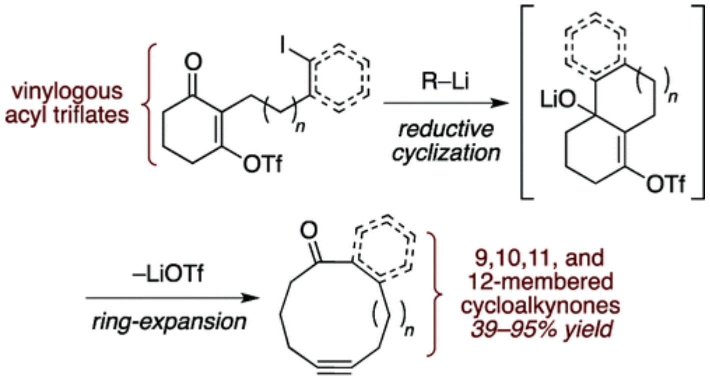
- Double C–H Activation: The Palladium-Catalyzed Direct C-Arylation of Xanthines with Arenes
  Malakar, C. C.; Schmidt, D.; Conrad, J.; Beifuss, U. *Org. Lett.* **2011**, *13*,1378–1381.
  Abstract:



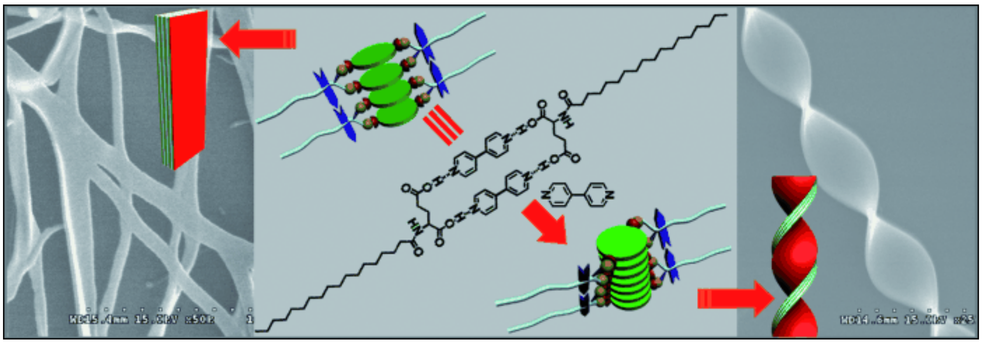
The novel Pd-catalyzed C(sp^2)–H/C(sp^2)–H cross-coupling of unactivated xanthines with unactivated arenes utilizing a combination of Ag(I) and O_2 as oxidants exclusively yields C-8 arylated xanthines in a single synthetic operation.

- Generation of Medium-Ring Cycloalkynes by Ring Expansion of Vinylogous Acyl Triflates
  Tummatorn, J.; Dudley, G. B. *Org. Lett.* **2011**, *13*, 1572–1575.
  Abstract:



Reductive cyclization of aryl and vinyl iodides tethered to vinylogous acyl triflates (VATs) induces a ring-expanding fragmentation to provide cyclic alkynyl ketones, including strained nine-membered cycloalkynes, in fair to excellent yield. The tandem cyclization/C–C bond-cleavage is initiated under carefully optimized conditions by halogen–metal exchange in the presence of carbonyl and vinyl triflate functionality. A modified protocol for alkylation of 1,3-cyclohexanedione is described for preparing the relevant VAT substrates.

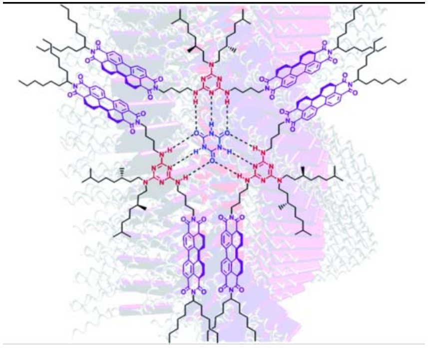
- Regulation of the Chiral Twist and Supramolecular Chirality in Co-Assemblies of Amphiphilic L-Glutamic Acid with Bipyridines
  Zhu, X.; Duan, P.; Zhang, L.; Liu, M. *Chem.-Eur. J.* **2011**, *17*, 3429-3437.
  Abstract:

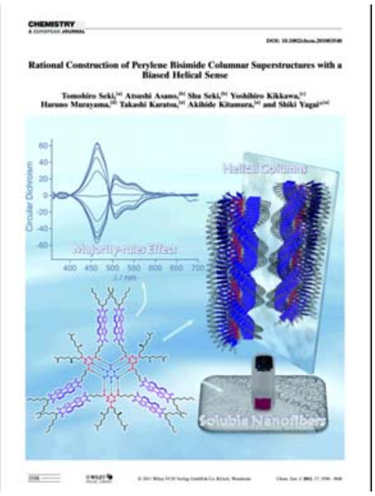


A series of amphiphilic L-glutamic acid derivatives with various saturated alkyl chains has been designed and their co-assembly with 4,4′-bipyridine in aqueous media has been investigated. While

the individual amphiphiles formed hydrogels with water and self-assembled into fine fiber networks, the addition of 4,4′-bipyridine caused significant changes in the co-assembled nanostructures such that twisted chiral ribbons were formed. In these supramolecular systems, either fine structural changes or adjustment of the stoichiometric ratio of the two components had crucial effects on the formation of the chiral twists. Based on detailed investigations by SEM and XRD analyses, FTIR, CD, and UV/Vis spectroscopies, and molecular simulation, it is considered that a delicate synergistic balance between π–π stacking, hydrophobic, and chiral interactions is responsible for the formation of the chiral twists. An interesting sandwich structure, in which an excess of 4,4′-bipyridine is inserted into the space of primary cages constructed from the amphiphile and 4,4′-bipyridine, is proposed. Remarkably, the handedness of these chiral twists is related not only to the chiral center of the glutamic unit, but also the chain length of the alkyl tails. This work provides a deeper understanding of the formation mechanism of chiral twists, and exemplifies a feasible shortcut to the rational design of chiral structures from basic molecular structures to supramolecular systems.

- Rational Construction of Perylene Bisimide Columnar Superstructures with a Biased Helical Sense
  Seki, T.; Asano, A.; Seki, S.; Kikkawa, Y.; Murayama, H.; Karatsu, T.; Kitamura, A.; Yagai, S. *Chem.-Eur. J.* **2011**, *17*, 3598-3608.
  <u>Abstract:</u>





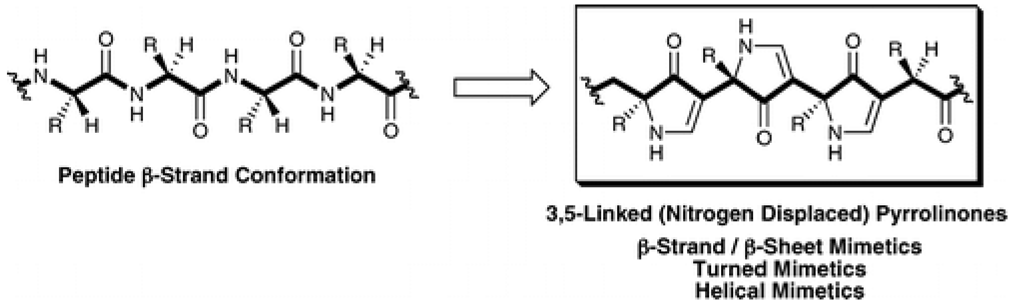
CHEMISTRY

Rational Construction of Perylene Bisimide Columnar Superstructures with a Biased Helical Sense

Tomohiro Seki, Atsushi Asano, Shu Seki, Yoshihiro Kikkawa, Haruno Murayama, Takashi Karatsu, Akihide Kitamura, and Shiki Yagai

Discotic supramolecular complexes bearing six perylene bisimide (PBI) chromophores were prepared by mixing monotopically triple-hydrogen-bonding melamines equipped with two PBI chromophores and two 3,7-dimethyloctyl chiral handles with tritopically triple-hydrogen-bonding cyanuric acid (CA). UV/Vis and fluorescence titration experiments demonstrated that the discotic complexes were formed in methylcyclohexane by the 3:1 complexation between the melamines and CA. TEM and AFM studies revealed that the complexes hierarchically organize into fibrous columnar assemblies, which eventually results in the formation of organogels. Circular dichroism (CD) and flash-photolysis time resolved microwave conductivity measurements revealed the presence of extended chiral stacks of PBI chromophores within the columns. The anisotropy factors of the columnar assemblies are remarkably high (g=1.5×10^{-3}) when considering the presence of only one 3,7-dimethyloctyl chiral handle per perylene chromophore, suggesting that the columnar structures have a biased helical sense. The fact that the chiral centers are located inside the discotic complexes rather than at their peripheries might be unique structural property responsible for the rather strong optical activities for the assemblies of this chromophore. The effective transcription of the molecular chirality to the extended columnar assemblies through the formation of unique discotic complexes enables the expression of "majority-rules" chiral amplification effect, which is unprecedented for the supramolecular assemblies of PBIs.

- Pyrrolinone-Based Peptidomimetics. "Let the Enzyme or Receptor be the Judge"
  Smith, III, A. B.; Charnley, A. K.; Hirschmann, R. *Acc. Chem. Res.* **2011**, *44*, 180–193.
  Abstract:

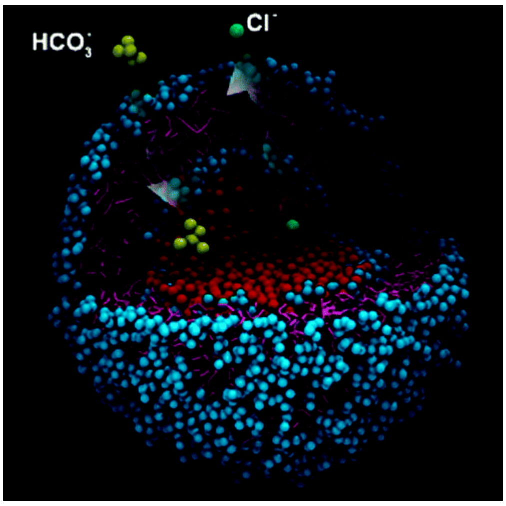


Peptides and proteins, evolved by nature to perform vital biological functions, would constitute ideal candidates for therapeutic intervention were it not for their generally poor pharmacokinetic profiles. Nonpeptide peptidomimetics have thus been pursued because they might overcome these limitations while maintaining both the potency and selectivity of the parent peptide or protein. Since the late 1980s, we have sought to design, synthesize, and evaluate a novel, proteolytically stable nonpeptide peptidomimetic scaffold consisting of a repeating structural unit amenable to iterative construction; a primary concern is maintaining both the appropriate peptide-like side-chains and requisite hydrogen bonding. In this Account, we detail how efforts in the Smith−Hirschmann laboratories culminated in the identification of the 3,5-linked polypyrrolinone scaffold.

We developed effective synthetic protocols, both in solution and on solid supports, for iterative construction of diverse polypyrrolinones that present functionalized peptide-like side-chains. As a result of the rigid nature of the pyrrolinone scaffold, control over the backbone conformation could be exerted by modulation of the stereogenicity of the constituent monomers and the network of intramolecular hydrogen bonding. The extended conformation of the homochiral 3,5-linked polypyrrolinone scaffold proved to be an excellent mimic for β-strands and β-sheets. Application to enzyme inhibitor design and synthesis led not only to modest inhibitors of the aspartic acid protease renin and the matrix metalloprotease class of enzymes, but importantly to bioavailable HIV-1 protease inhibitors with subnanomolar binding constants.

The design and synthesis of a competent peptide−pyrrolinone hybrid ligand for the class II major histocompatibility complex (MHC) antigen protein HLA-DR1 further demonstrated the utility of the 3,5-polypyrrolinone motif as a mimic for the extended polyproline type II peptide backbone. Equally important, we sought to define, by synthesis, the additional conformational space accessible to the polypyrrolinone structural motif, with the ultimate goal of accessing pyrrolinone-based turn and helix mimetics. Toward this end, a mono-N-methylated bispyrrolinone was found to adopt an extended helical array in the solid state. Subsequent synthesis of d,l-alternating (heterochiral) tetrapyrrolinones both validated the expected turn conformations in solution and led to a functionally active mimetic of a peptidal β-turn (similar to somatostatin). Finally, the design, synthesis, and structural evaluation of both acyclic and cyclic heterochiral (that is, d,l-alternating) hexapyrrolinones yielded nanotube-like assemblies in the solid state. Taken together, these results illustrate the remarkable potential of the 3,5-linked polypyrrolinone scaffold as β-strand, β-sheet, β-turn, and potentially helical peptidomimetics.

- From Anion Receptors to Transporters
  Gale, P. A. *Acc. Chem. Res.* **2011**, *44*, 216–226.
  Abstract:



Cystic fibrosis is the most well-known of a variety of diseases termed channelopathies, in which the regulation of ion transport across cell membranes is so disrupted that the threshold of a pathology is passed. The human toll exacted by these diseases has led a number of research groups, including our own, to create compounds that mediate ion transport across lipid bilayers.

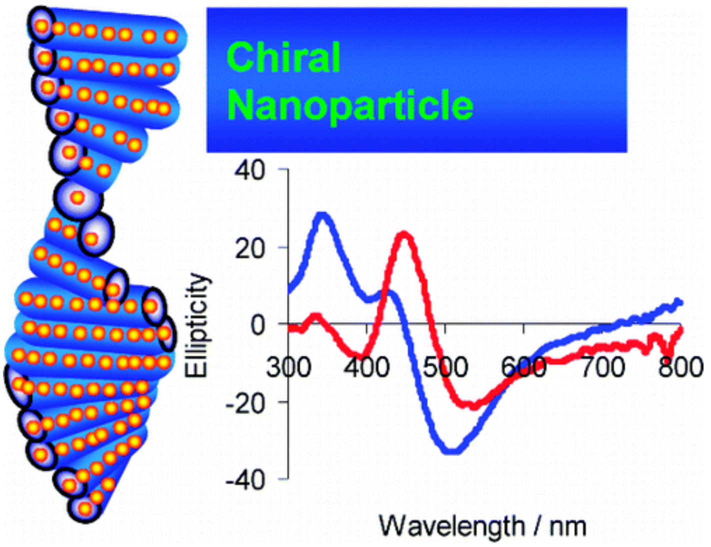
In this Account, we discuss three classes of synthetic compounds that were refined to bind and transport anions across lipid bilayer membranes. All of the compounds were originally designed as anion receptors, that is, species that would simply create stable complexes with anions, but were then further developed as transporters. By studying structurally simple systems and varying their properties to change the degree of preorganization, the affinity for anions, or the lipophilicity, we have begun to rationalize why particular anion transport mechanisms (cotransport or antiport processes) occur in particular cases. For example, we have studied the chloride transport properties of receptors based on the closely related structures of isophthalamide and pyridine-2,6-dicarboxamide: the central ring in each case was augmented with pendant methylimidazole groups designed to cotransport H^+ and Cl^-. We observed that the more preorganized pyridine-based receptor was the more efficient transporter, a finding replicated with a series of isophthalamides in which one contained hydroxyl groups designed to preorganize the receptor. This latter class of compound, together with the natural product prodigiosin, can transport bicarbonate (as part of a chloride/bicarbonate antiport process) across lipid bilayer membranes.

We have also studied the membrane transport properties of calix[4]pyrroles. Although the parent meso-octamethylcalix[4]pyrrole functions solely as a Cs^{+}/Cl^{-} cotransporter, other compounds with increased anion affinities can function through an antiport process. One example is octafluoro-meso-octamethylcalix[4]pyrrole; with its electron-withdrawing substituents, it can operate through a chloride/bicarbonate antiport process. Moreover, calix[4]pyrroles with additional hydrogen bond donors can operate through a chloride/nitrate antiport process. Thus, increasing the affinity of the receptor in these cases allows the compound to transport an anion in the absence of a cation.

Finally, we have studied the transport properties of simple thioureas and shown that these compounds are highly potent chloride/bicarbonate antiport agents that function at low concentrations. In contrast, the urea analogues are inactive. The higher hydrophobicity (reflected in higher values for the logarithm of the water−octanol partition constant, or log P) and lower polar

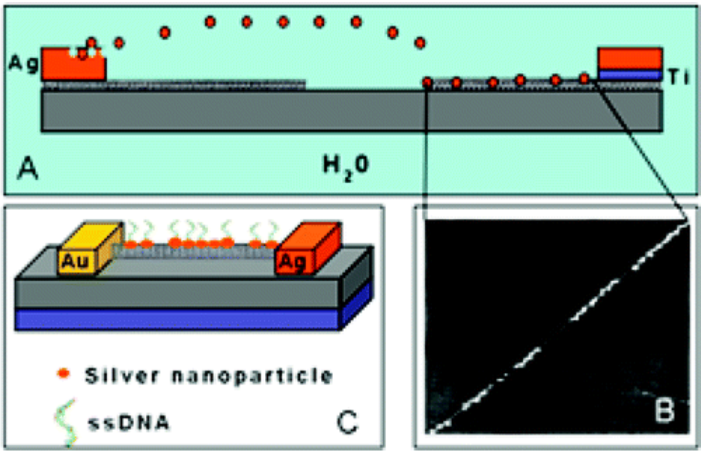
surface areas of the thiourea compounds compared to their urea analogues may provide a clue to the high potency of these compounds. This observation might serve as a basis for designing future small-molecule transporters.

- Chiral Nematic Assemblies of Silver Nanoparticles in Mesoporous Silica Thin Films
  Qi, H.; Shopsowitz, K. E.; Hamad, W. Y.; MacLachlan, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 3728–3731.
  Abstract:



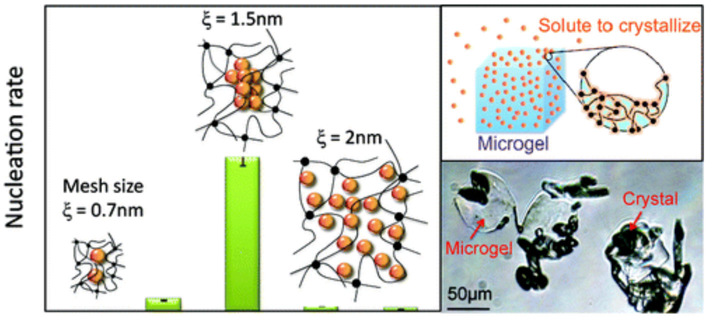
Silver nanoparticles (NPs) have been synthesized inside mesoporous silica films with chiral nematic structure. Circular dichroism measurements of the silver NP-loaded silica films show NP-based optical activity in the vicinity of the surface plasmon resonance. These materials, with an optical response associated with the chiral assembly of metal NPs, may be useful for developing new sensors.

- Controlled Assembly of Ag Nanoparticles and Carbon Nanotube Hybrid Structures for Biosensing
  Sahoo, S.; Husale, S.; Karna, S.; Nayak, S. K.; Ajayan, P.M. *J. Am. Chem. Soc.* **2011**, *133*, 4005–4009.
  Abstract:



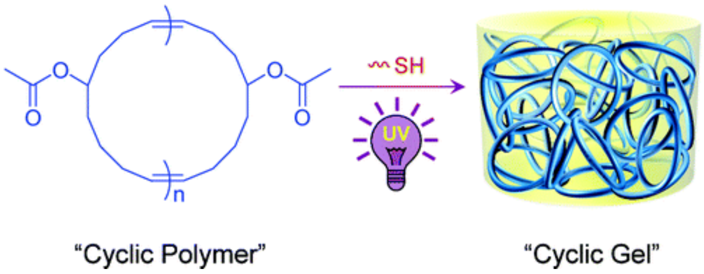
Here we report a chemical-free, simple, and novel method in which a part from a silver-based anode is controllably used in a straightforward manner to produce silver nanoparticles (Ag NPs) in order to fabricate a controlled assembly of Ag NPs and single walled carbon nanotube (SWCNT) hybrid structures. The attachment and distribution of Ag NPs along SWCNTs have been investigated and characterized by field emission scanning electron microscopy (FESEM). We have achieved the decoration of SWCNTs with different densities of Ag NPs by changing the deposition time, the applied voltage, and the location of carbon nanotubes with respect to the anode. At low voltage, single silver nanoparticle is successfully attached at the open ends of SWCNTs whereas at high voltage, intermediate and full coverage densities of Ag NPs are observed. As voltage is further increased, fractals of Ag NPs along SWCNTs are observed. In addition, a device based on a Ag NPs−SWNT hybrid structure is used for the label-free detection of ssDNA molecules immobilized on it. We believe that the proposed method can be used to decorate and/or assemble metal nanoparticles or fractal patterns along SWCNTs with different novel metals such as gold, silver, and copper and can be exploited in various sensitive applications for fundamental research and nanotechnology.

- Controlled Nucleation from Solution Using Polymer Microgels
  Diao, Y.; Helgeson, M. E.; Myerson, A. S.; Hatton, T. A.; Doyle, P. S.; Trout, B. L. *J. Am. Chem. Soc.* **2011**, *133*, 3756–3759.
  Abstract:



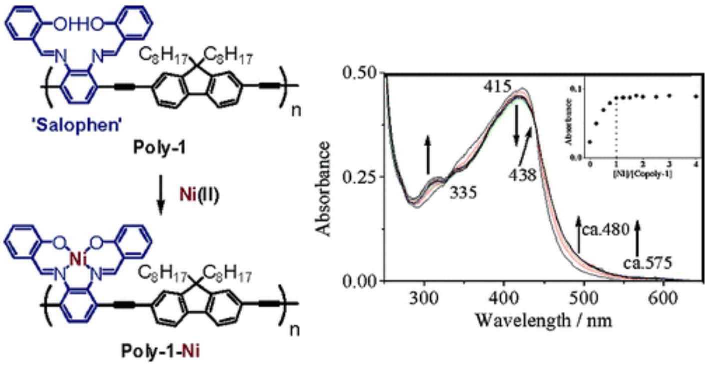
Despite its widespread occurrence in nature and broad application in industrial practice, nucleation of crystalline materials remains largely unpredictable and therefore difficult to control. In this work, we demonstrate a new method to control nucleation with polymer microgels by tuning their microstructure to vary systematically the degree of nanoscopic confinement and its effects on nucleation. We find that the polymer microstructure has a significant impact on nucleation kinetics. Moreover, there exists an optimum polymer mesh size at which the rate of nucleation is dramatically enhanced, the degree to which depends on the extent of polymer−solute interactions. With easily tunable microstructure and chemistry, polymer microgels offer a promising approach for the rational design of materials for controlling nucleation from solution.

- Gels Based on Cyclic Polymers
  Zhang, K.; Lackey, M. A.; Cui, J.; Tew, G. N. *J. Am. Chem. Soc.* **2011**, *133*, 4140–4148.
  Abstract:



Cyclic poly(5-hydroxy-1-cyclooctene) (PACOE) was synthesized by ring-expansion metathesis polymerization (REMP), and thiol−ene chemistry was used to cross-link the internal double bonds in the PACOE backbone. This created a novel network material (gels formed from cyclic polymers) with unique structural units, where the cyclic PACOE main chains, which serve as secondary topological cross-linkages, were connected by primary intermolecular chemical cross-linkages. The resulting properties were notably different from those of traditional chemically cross-linked linear PACOE gels, whose gel fraction (GF) and modulus (G) increased while the swelling ratio (Q) decreased with increasing initial polymer concentration in the gel precursor solution (C0). For the gels formed from cyclic polymers, however, the GF, Q, and G all simultaneously increased as C0 increased at the higher range. Furthermore, at the same preparation state (same C0), the swelling ability and the maximum strain at break of the gels formed from cyclic polymers were always greater than those of the gels formed from linear polymers, and these differences became more pronounced as C0 increased.

- π-Conjugated Poly(aryleneethynylene)s Consisting of Salophen and Ni−Salophen Units in the π-Conjugated Main Chain: Preparation and Chemical Properties
  Fukumoto, H.; Yamane, K.; Kase, Y.; Yamamoto, T. *Macromolecules* **2010**, *43*, 10366–10375.
  Abstract:

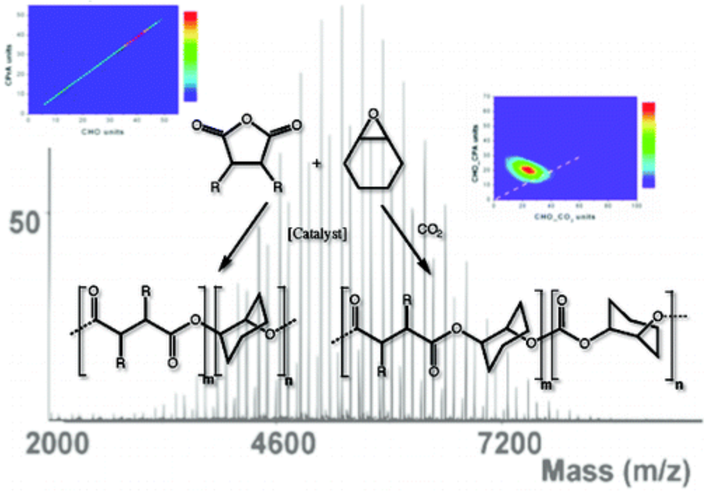


π-Conjugated poly(aryleneethynylene)s consisting of *N*,*N*⍰-bis(salicylidene)-1,2-phenylenediamine (salophen) units (**Poly-1**−**Poly-3**) and salophen−nickel complex units (**Poly-1−Ni**) were prepared in high yields by the palladium-catalyzed polycondensation of H−⍰−Ar−⍰−H (Ar = fluorene or 2,5-dialkoxy-*p*-phenylene) with dibromo compounds of salophen (**Br2−Salophen**) and its nickel complex (**Br2−Salophen−Ni**), respectively. The Ni-free polymers (**Poly-1**−**Poly-3**) showed good solubility in $CHCl_3$ and THF, had high thermal stability, and exhibited number-average molecular weights (M_n) of 9200−14000 in GPC analysis. The UV−vis spectra of the polymers showed π−π* transition peaks at about 420 nm, which was comparable to those of poly(*p*-phenyleneethynylene)s. The UV−vis spectrum of **Poly-1−Ni** exhibited additional intermediate and small peaks at about 480 and 600 nm, which were assigned to a charge-transfer (CT) electronic transition and a d−d transition, respectively. The complexation of **Poly-1** with Ni^{2+} proceeded clearly and quantitatively to give **Poly-1−Ni**, as monitored by UV−vis spectroscopy. Both the Ni-free and Ni-containing polymers were electrochemically active, and CV (cyclic volammetry) scans of the polymers showed a reduction peak of the salophene unit at approximately −2.2 V vs Ag^+/Ag and an oxidation peak of the salophene unit at about 0.8 V vs Ag^+/Ag.

- Ring-Opening Co- and Terpolymerization of an Alicyclic Oxirane with Carboxylic Acid Anhydrides and CO_2 in the Presence of Chromium Porphyrinato and Salen Catalysts

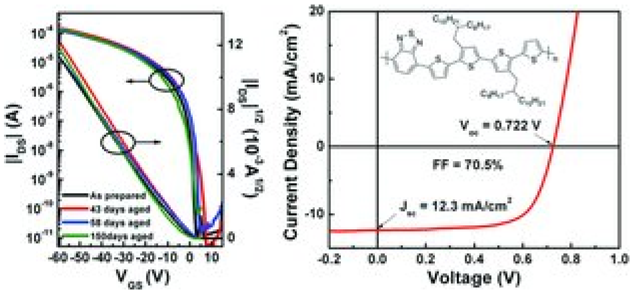
Huijser, S.; HosseiniNejad, E.; Sablong, R.; de Jong, C.; Koning, C. E.; Duchateau, R. *Macromolecules* **2011**, *44*, 1132–1139.

Abstract:



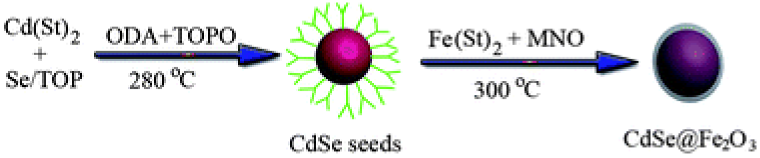
Copolymerization of cyclohexene oxide (CHO) with alicyclic anhydrides applying chromium tetraphenylprophyrinato (TPPCrCl, **1**) and salophen (SalophenCrCl, **2**) catalysts resulted in polyesters or poly(ester-*co*-ether)s, depending on the nature of the catalyst, presence of a cocatalyst, solvent and type of anhydride. The combination of **1** as catalyst and 4-*N*,*N*-dimethylamino-pyridine (DMAP) as cocatalyst in the copolymerization of CHO with succinic anhydride (SA), cyclopropane-1,2-dicarboxylic acid anhydride (CPrA), cyclopentane-1,2-dicarboxylic acid anhydride (CPA) or phthalic anhydride (PA) invariably resulted in a completely alternating topology and therefore a pure polyester. Contrarily, **2** in combination with DMAP did not afford pure polyesters for the copolymerization of CHO with SA or CPrA but did render the alternating topology when CPA or PA was used as anhydride comonomer. Water proved to be an efficient bifunctional CTA affording α,ω-hydroxyl-terminated polyesters without loss of catalytic activity. When CO_2 was introduced as additional monomer to CHO and the anhydrides, both **1** and **2** in combination with DMAP as cocatalyst afforded perfect poly(ester-*co*-carbonate)s. The presence of CO_2 effectively prevents the undesirable side reaction of oxirane homopolymerization.

- A Versatile Low Bandgap Polymer for Air-Stable, High-Mobility Field-Effect Transistors and Efficient Polymer Solar Cells
  Ong, K.-H.; Lim, H.-S.; Tan, H.-S.; Wong, H.-K.; Li, J.; Ma, Z.; Moh, L. C. H.; Lim, S.-H., De Mello, J. C.; Chen, Z.-K. *Adv. Mater.* **2011**, *23*, 1409-1413.
  Abstract:



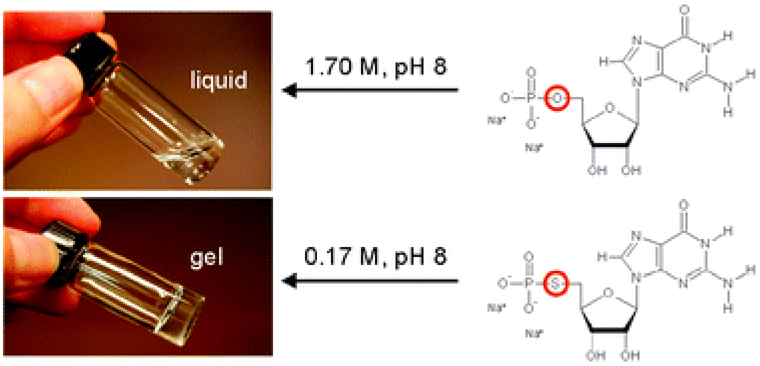
A new low bandgap polymer POD2T-DTBT has been synthesized and found to give excellent performances in organic thin-film transistor (OTFT) and organic photovoltaic (OPV) applications. OTFTs based on POD2T-DTBT have achieved good hole carrier mobilities of 0.2 $cm^2V^{-1}s^{-1}$ and OPVs based on blends of POD2T-DTBT and $PC_{71}BM$ have demonstrated promising power conversion efficiencies of 6.26%.

- Bifunctional nanoparticles with superparamagnetic and luminescence properties
  Zhan, F.; Zhang, C. Y. *J. Mater. Chem.*, **2011**, *21*, 4765-4767.
  Abstract:



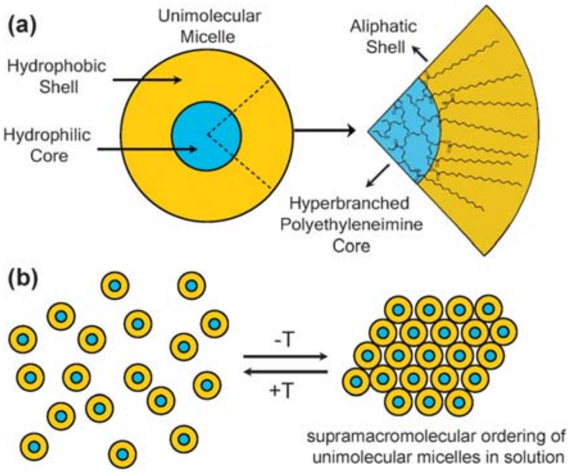
We report for the first time the synthesis of $CdSe@Fe_2O_3$ core/shell nanoparticles by a one-step seeded-growth approach. These nanoparticles not only retain their individual semiconducting and magnetic functionalties, but also exhibit some new properties which are affected by the coating components. These bifunctional $CdSe@Fe_2O_3$ nanoparticles might find potential applications in biosensing and in biomedical research.

- Single atom modification leads to enhanced nucleotide self-assembly: the role of cation bridging
  Kwan, I. C. M.; Delley, R. J.; Hodgson, D. R. W.; Wu, G. *Chem. Commun.* **2011**, *47*, 3882-3884.
  Abstract:



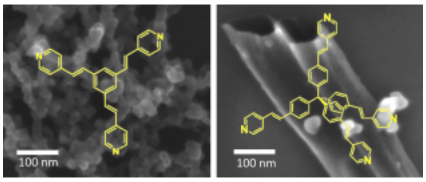
We report that the ability of disodium 5′-deoxy-5′-thioguanosine-5′-monophosphate, Na_2 (5′-GSMP), to self-associate into a helical G-quadruplex structure in aqueous solution at pH 8 is significantly higher than that of disodium guanosine-5′-monophosphate, Na_2(5′-GMP), which supports our earlier hypothesis regarding the importance of cation bridging.

- Thermoreversible formation and negative thermal expansion of supramacromolecular assemblies of unimolecular micelles in solution
  Picco, A. S.; Yameen, B.; Azzaroni, O.; Ceolín, M. *Chem. Commun.* **2011**, *47*, 3802-3804.
  Abstract:



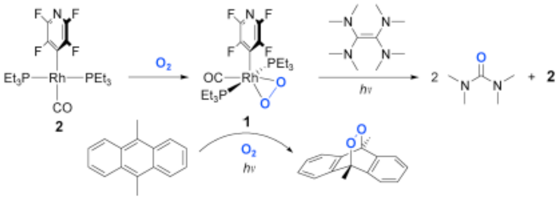
We report the thermoreversible formation of superstructural assemblies of unimolecular micelles in solution displaying negative thermal expansion behaviour.

- Coordination-Polymer Nanotubes and Spheres: A Ligand-Structure Effect
  Kaminker, R.; Popovitz-Biro, R.; van der Boom, M. E. *Angew. Chem. Int. Ed.* **2011**, *50*, 3224-3226.
  <u>Abstract:</u>



Ball or tube: Flexible and amorphous nanotubes were generated with a palladium salt and a multidentate ligand having a tetrahedral structure (right). In contrast, regardless of the number of metal coordination sites, ligands with a two-dimensional geometry lead to the formation of spheres and their aggregates (left).

- A Rhodium Peroxido Complex in Mono-, Di-, and Peroxygenation Reactions
  Meier, G.; Braun, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 3280-3284.
  <u>Abstract:</u>



A versatile peroxido complex: The rhodium peroxido complex **1**, which can be prepared from **2** and dioxygen, participates in mono-oxygenation of a phosphine and dioxygenation of tetrakis(dimethylamino)ethylene to give, respectively, phosphine oxide and a urea derivative, while peroxygenation of 9,10-dimethylanthracene to yield the anthracene endoperoxide takes place in the presence of dioxygen and substoichiometric amounts of **1** (see scheme).